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Pyrographic Characterization of Municipal Waste

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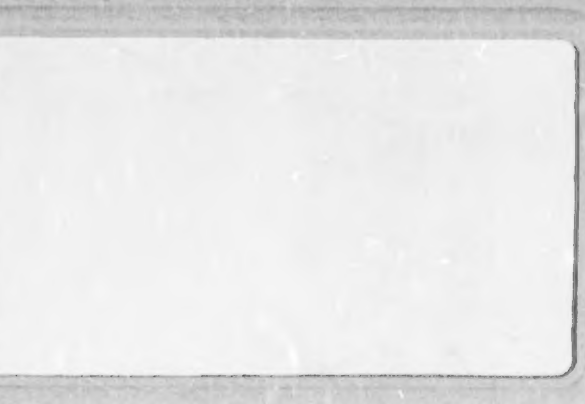

Rocketdyne
North American Rockwell

6633 Canoga Avenue
Canoga Park, California 91304

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PYROGRAPHIC CHARACTERIZATION OF MUNICIPAL WASTE

by

I. Lysyj and K. H. Nelson

for

The Advanced Waste Treatment Research Laboratory

Robert A. Taft Water Research Center

This report is submitted in fulfillment of Contract No. 14-12-545 between the Federal Water Pollution Control Administration and Rocketdyne.

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FOREWORD

In its assigned function as the Nation's principal natural resource agency, the United States Department of the Interior bears a special obligation to ensure that our expendable resources are conserved, that renewable resources are managed to produce optimum yields, and that all resources contribute their full measure to the progress, prosperity, and security of America -- now and in the future.

This series of reports has been established to present the results of intramural and contract research studies carried out under the guidance of the technical staff of the FWPCA Robert A. Taft Water Research Center for the purpose of developing new or improved wastewater treatment methods. Included is work conducted under cooperative and contractual agreements with Federal, State, and local agencies, research institutions, and industrial organizations. The reports are published essentially as submitted by the investigators. The ideas and conclusions presented are, therefore, those of the investigators and not necessarily those of the FWPCA.

Reports in this series will be distributed as supplies permit. Requests should be sent to the Office of Information, Ohio Basin Region, Federal Water Pollution Control Administration, 4676 Columbia Parkway, Cincinnati, Ohio 45226.

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TABLE OF CONTENTS

Foreword ii
Acknowledgement iii
Abstract vi
Introduction 1
Experimental 3
  Pyrographic Apparatus 3
  Performance Verification 5
Pyrolysis of Municipal Waste 11
  Experimental 11
  Results and Discussion 11
Conclusions and Recommendations 25
References 26

ILLUSTRATIONS

1. Flow Diagram Showing Relationship of Components in the Breadboard Pyrographic Apparatus 4
2. Pyrogram of 80 ppm Solution of t-Butyl Alcohol 6
3. Pyrogram of 80 ppm Methyl Isobutyl Ketone in Water 7
4. Pyrogram of 93 ppm Solution of Hexanoic Acid 8
5. Pyrogram of 100 ppm dl-Valine in Water 9
6. Pyrogram of Raw Sewage 10 July 1969 12
7. Pyrogram of Primary Effluent 10 July 1969 13
8. Pyrogram of Secondary Effluent 10 July 1969 14
9. Pyrogram of Tertiary Effluent 10 July 1969 14
10. Pyrogram of Raw Sewage 16 July 1969 17
11. Pyrogram of Primary Effluent 16 July 1969 18
12. Pyrogram of Secondary Effluent 16 July 1969 19
13. Pyrogram of Tertiary Effluent 16 July 1969 19
14. Pyrogram of Enriched Sewage 16 July 1969 23

TABLES

I. Retention Times of Pyrographic Peaks for Pomona Water Renovation Plant Samples Secured on 10 July 1969 16
II. Retention Times of Pyrographic Peaks for Pomona Water Renovation Plant Samples Obtained on 16 July 1969 20
III. Calculated Organic Loads for Pyrolyzed Municipal Waste Samples 22
IV. Comparison of Pyrographic Peaks for Raw Sewage and Enriched Sewage 24

ABSTRACT

This three-month program was a limited study of the feasibility of applying the pyrographic analytical technique to the characterization of municipal waste as it passes through a treatment plant. The pyrographic method is based on (1) pyrolysis of the waste in the presence of water, (2) separation of the resulting organic pyrolytic products with a gas chromatographic column, (3) measurement of the eluted products with a hydrogen flame ionization detector, and (4) analysis of the pyrogram.

For this program, a breadboard pyrographic apparatus, which was initially assembled and used in 1967, was reactivated. Aqueous solutions of several different organic compounds were pyrolyzed to establish operating conditions and to verify the performance of the apparatus. Then samples of raw sewage and primary, secondary, and tertiary effluents from the Pomona Water Renovation Plant were pyrolyzed. The complexity of the pyrograms decreased as the wastewater passed through the plant.

INTRODUCTION

Although identification of specific organics in wastewater can be undertaken with specialized procedures developed for particular situations, such specific methods for routine analysis of waste treatment effluents are time consuming and do not lend themselves to effective plant operational control. To deal effectively with problems of process control in treatment plants, a methodology capable of gross characterization of the organic materials would be desirable. For process control purposes, it may be sufficient to characterize changes in chemical composition of wastewater in terms of chemical groups or classes. The determination of individual compounds may not be necessary. However, such a methodology must be capable of indicating changes in wastewater through all stages of treatment including primary, secondary, and tertiary steps. A pyrographic method for conducting organic analysis in water by group characterization appeared applicable to tracing the fate of organics through the various stages of a waste treatment process.

The development of a pyrographic technique for characterizing classes of organics has been underway since 1963. The design of an apparatus for the direct analysis of nonvolatile organics in aqueous solutions has been reported (1). This instrumentation, which was assembled from commercially available equipment, consisted of a gas chromatograph equipped with a flame ionization detector, a tubular pyrolysis chamber heated by a microcombustion furnace, a custom-built sample injector, and a recorder. The source of hydrogen was either a hydrogen generator or a cylinder of hydrogen. Steam was used as a carrier gas because it permitted the injection of large samples with a consequent increase in the overall sensitivity of the procedure.

Using this apparatus, the direct analysis for the organic content of natural waters was performed (2). In this application, high temperature pyrolysis of organics was conducted in the presence of the water yielding methane, hydrogen, and other small molecular fragments. The pyrolytic products passed through a glass bead column without separation and were measured as a single peak by a flame ionization detector. The procedure was calibrated with solutions similar in composition to the waters being analyzed.

The first pyrographic differentiation between different organic materials present in water was reported by Lysyj, Nelson and Newton (3). This technique was based on the observation that the major organic materials derived from natural sources are quite deficient in methylene and methyl groups. These materials are either highly oxygenated or contain nitrogen functional groups. Many industrial pollutants, on the other hand, such

as hydrocarbons, alkyl alcohols, and others contain a high percentage of methylene and methyl groups. Therefore, the pyrolysis process was modified to optimize the production of methane so as to distinguish between industrial pollutants and naturally occurring compounds. In addition, a gas chromatographic column was used which retained all products of pyrolysis except methane. With this differentiating procedure, very low blanks were obtained for natural water samples and for synthetic samples containing carbohydrates, polypeptides, and lipids. Methylated organic materials, on the other hand, produced a sufficiently high response to be detectable in water solution at low parts per million concentrations.

With the successful demonstration of the differentiating potential of the pyrographic technique, a more complex study directed towards pyrographic characterization of multicomponent organic mixtures in aqueous media was undertaken (4). In this study, the direct pyrolysis of water samples containing organic matter was combined with gas chromatography for separation of the pyrolytic fragments to permit the quantitative characterization of the aqueous sample. Steam was used as the carrier gas so that the addition of water vapor from the sample would have little or no effect on the performance of the hydrogen flame ionization detector. Three classes of organic materials were selected for this study - carbohydrates, polypeptides, and lipids. With the use of these materials, it was demonstrated that direct pyrolysis of water samples containing organic matter, when combined with gas chromatographic separation of the fragments produced, can be used for qualitative and quantitative characterization of aqueous solutions.

From these studies, a pyrographic approach for the direct analysis of organic wastes in water was evolved. The method is based on (1) pyrolysis of the waste in the presence of the water, (2) separation of the resulting pyrolytic organic fragments by means of a gas chromatographic column, (3) measurement of the eluted fractions with a hydrogen flame ionization detector, and (4) analysis of the resulting pyrograms. The feasibility of this approach has been verified in the analysis of multicomponent organic mixtures in aqueous media. A research program, with the objective of testing the feasibility of this concept for characterization of water contaminants in waterways, was initiated 30 June 1968 under the sponsorship of the Federal Water Pollution Control Administration, U. S. Department of the Interior. To date, this effort has progressed from engineering design and assembly of an advanced pyrographic instrument through laboratory testing to field tests.

In this report, the results are presented of a feasibility study of the applicability of pyrographic characterization techniques to the problems of process control in municipal waste treatment plants. This study was a limited, three-month program which utilized a breadboard pyrographic apparatus initially assembled and used in 1967.

EXPERIMENTAL

PYROGRAPHIC APPARATUS

For this program, a breadboard version of the pyrographic instrumentation, shown schematically in Figure 1, was reactivated. This instrumentation consisted of several subsystems which were a sampling system, a pyrolysis system, a chromatographic system, and the gas supply systems.

The sampling system was a Carle microvolume valve and a 10 cc Luer-Lok syringe. The valve had two sample loops so that the carrier gas could flow through one loop into the pyrolysis and chromatographic systems while the other loop was being filled with the water sample from the syringe. Subsequent rotation of the valve diverted the carrier gas through the second loop to transport the measured water sample into the pyrolysis chamber.

The pyrolysis system consisted of a pyrolysis chamber heated by a Lindberg Hevi-duty furnace which could be maintained at a stable pyrolysis temperature. The chamber was fabricated from an 11 inch length of 1/2 inch OD nickel tubing and Swagelok fittings. Short lengths of nickel wire filled the chamber.

The chromatographic system was a Hewlett-Packard Model 700 gas chromatograph equipped with a hydrogen flame ionization detector and a modified Hewlett-Packard 810 electrometer. A Hewlett-Packard 680 series strip chart recorder completed the system.

Two gas supply systems completed the instrumentation. These were the nitrogen carrier gas and the detector supply gases. The nitrogen carrier gas flowed sequentially through a filter, flowmeter, flow controller, and check valve to the sampling valve. From the sampling valve, the nitrogen flowed through the pyrolysis chamber and the chromatographic column to the detector. The detector gases were air and hydrogen. The air was supplied by an air pump and was filtered before entering the detector. The hydrogen flowed through a filter, flowmeter, and flow controller before entering the base of the detector. In the base, the hydrogen mixed with the nitrogen carrier gas before entering the jet of the detector.

The chromatographic column selected for this program was 50-80 mesh Porapak Q* in 8 ft. of 3/16 inch OD stainless steel tubing. This substrate had been used in the advanced pyrographic instrument designed for use in field studies. The substrate is stable, does not bleed, and provides suitable separation of many organic pyrolytic fragments derived from various wastes.

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* A product of Waters Associates, Framingham, Mass.

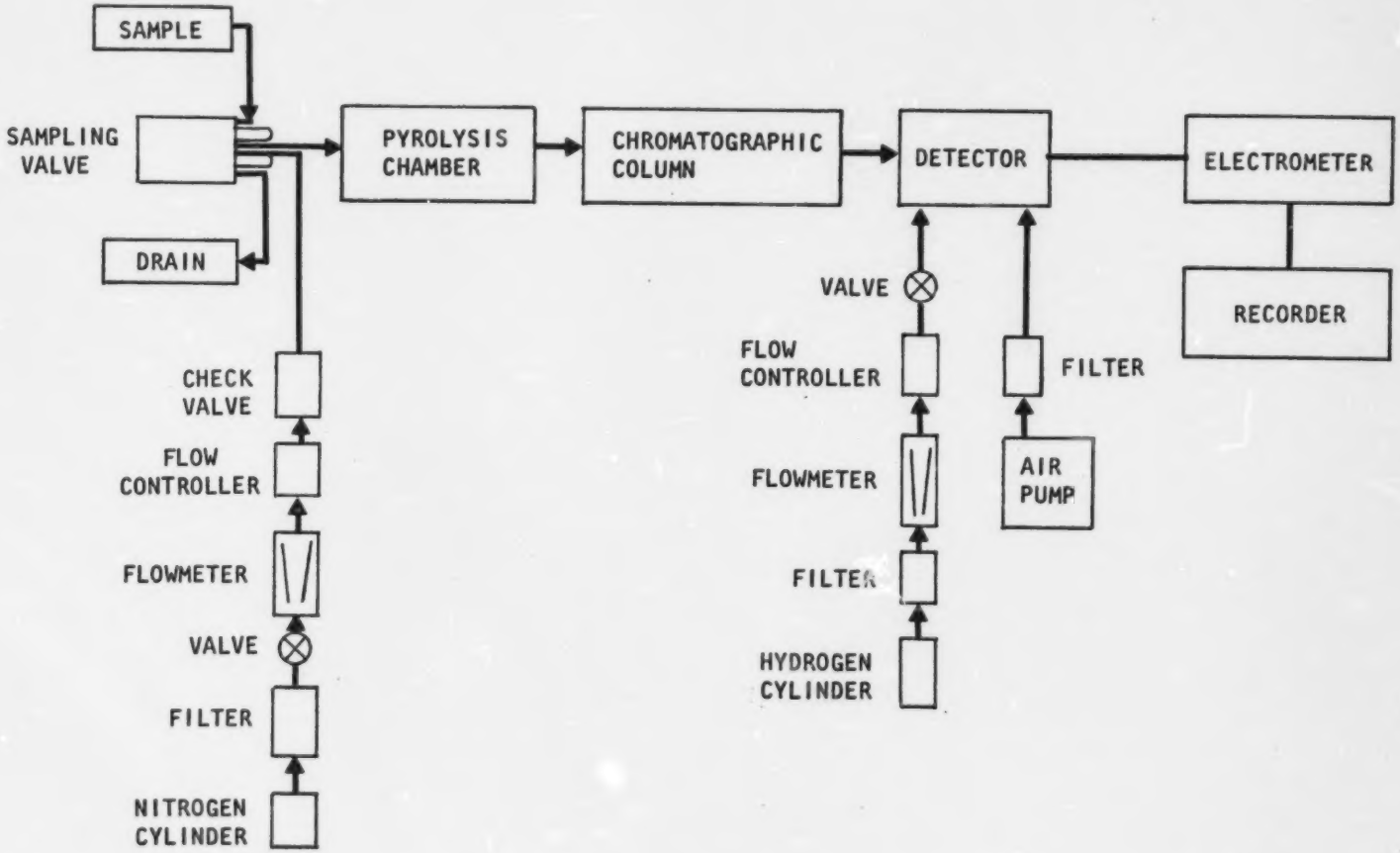

Figure 1. Flow Diagram Showing Relationship of Components in the Breadboard Pyrographic Apparatus

Suitable operating conditions for the apparatus, as determined during performance verification, were:

Nitrogen Carrier Gas	63 cc/min., 30 psig
Hydrogen Gas	45 cc/min., 25 psig
Air	450 cc/min.
Pyrolysis Furnace Temperature	600 C
Chromatographic Column Temperature	120 C
Detector Temperature	140 C
Chart Speed	As required
Attenuation	As required

PERFORMANCE VERIFICATION

The performance of the breadboard pyrographic apparatus was verified by pyrolyzing aqueous solutions of several organic compounds. The compounds included acetone, isopropyl alcohol, hexanoic acid, t-butyl alcohol, dl-valine, and methyl isobutyl ketone. These organic materials had been pyrolyzed in both the breadboard apparatus and the advanced pyrographic instrument in the past. Distilled water was used for preparing the solutions which ranged in concentration from 80 to 100 ppm of an organic compound.

In order to select a pyrolysis temperature for the program, several of the solutions were pyrolyzed at 500, 600, 700, and 800 C. From examination of the pyrograms, it appeared that a pyrolysis temperature of 600 C would provide a good compromise between the types of peaks and the magnitude of the peaks. The pyrograms also indicated that satisfactory separation of the pyrolysis products would be attained with a chromatographic column temperature of 120 C.

Some typical examples of the pyrograms obtained at 600 C by injecting aqueous solutions of the organic compounds into the breadboard pyrographic apparatus are shown in Figures 2 through 5. Each solution was pyrolyzed several times to be certain a representative pyrogram was obtained. The pyrograms as reproduced in Figures 2 through 5 show only significant portions of gas chromatographic runs, i.e., no additional peaks appeared on the pyrogram of 80 ppm t-Butyl alcohol (Figure 2) after 29 minutes, therefore, the time scale for Figure 2 is 0-29 minutes. In the pyrogram of d,l-valine (Figure 5), on the other hand, a number of peaks appeared after 29 minutes. In order to reproduce all the pyrograms on the same page size, the time scale for Figure 5 was compressed to 0-46 minutes. In the type and relative magnitude of peaks, these pyrograms are similar to those obtained previously with the breadboard apparatus.

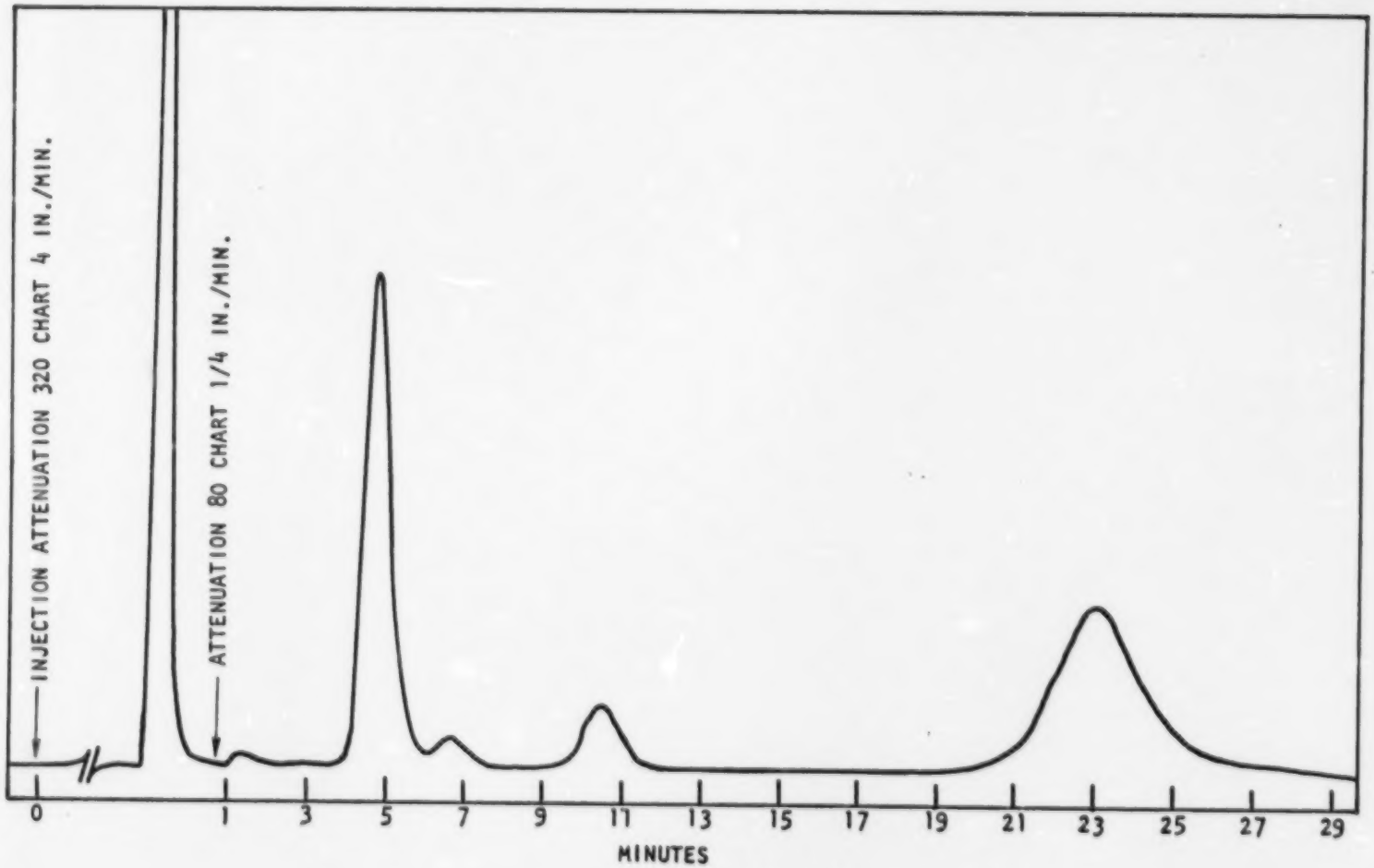

Figure 2. Pyrogram of 80 ppm Solution of t-Butyl Alcohol

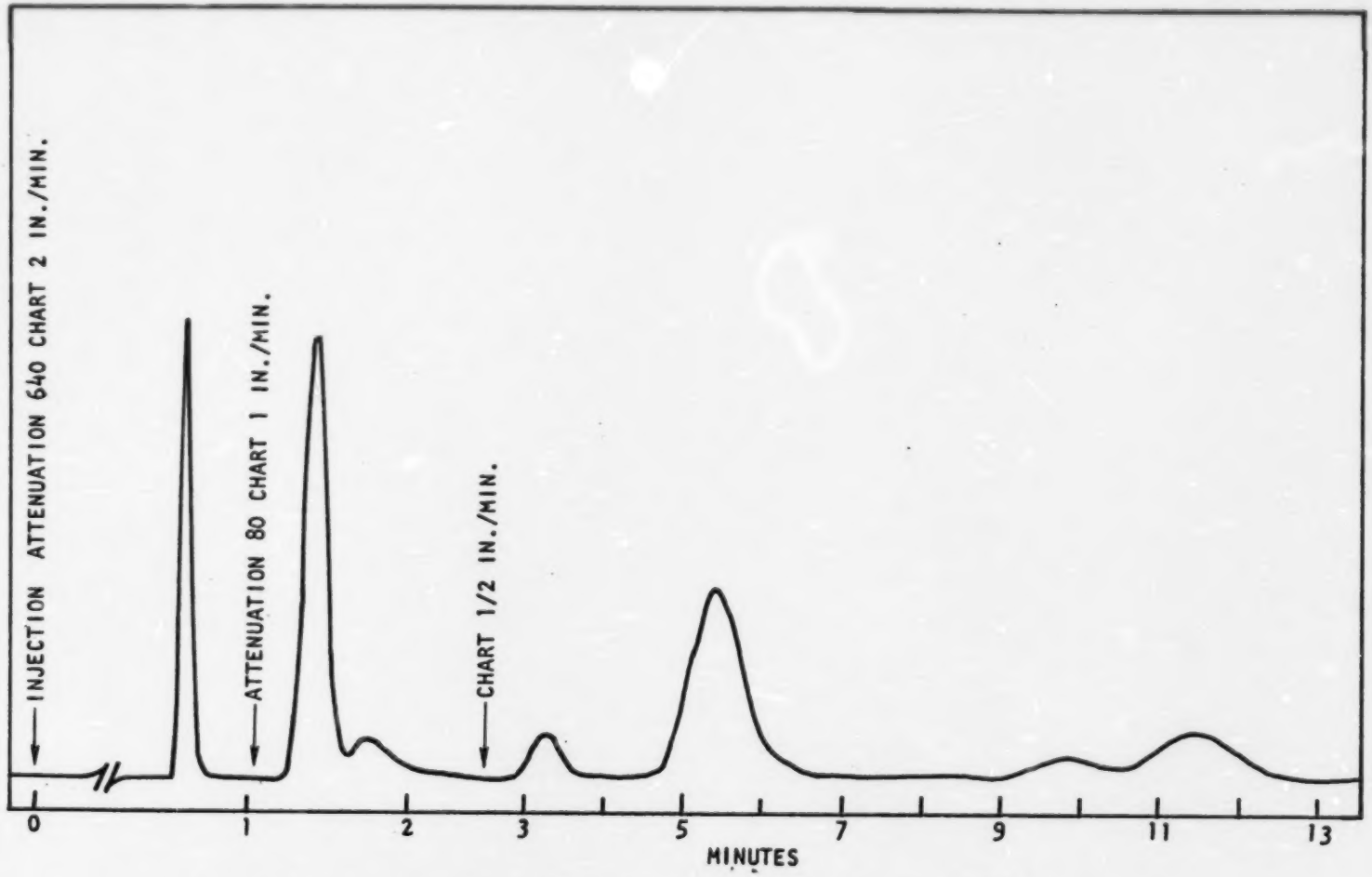

Figure 3. Pyrogram of 80 ppm Methyl Isobutyl Ketone in Water

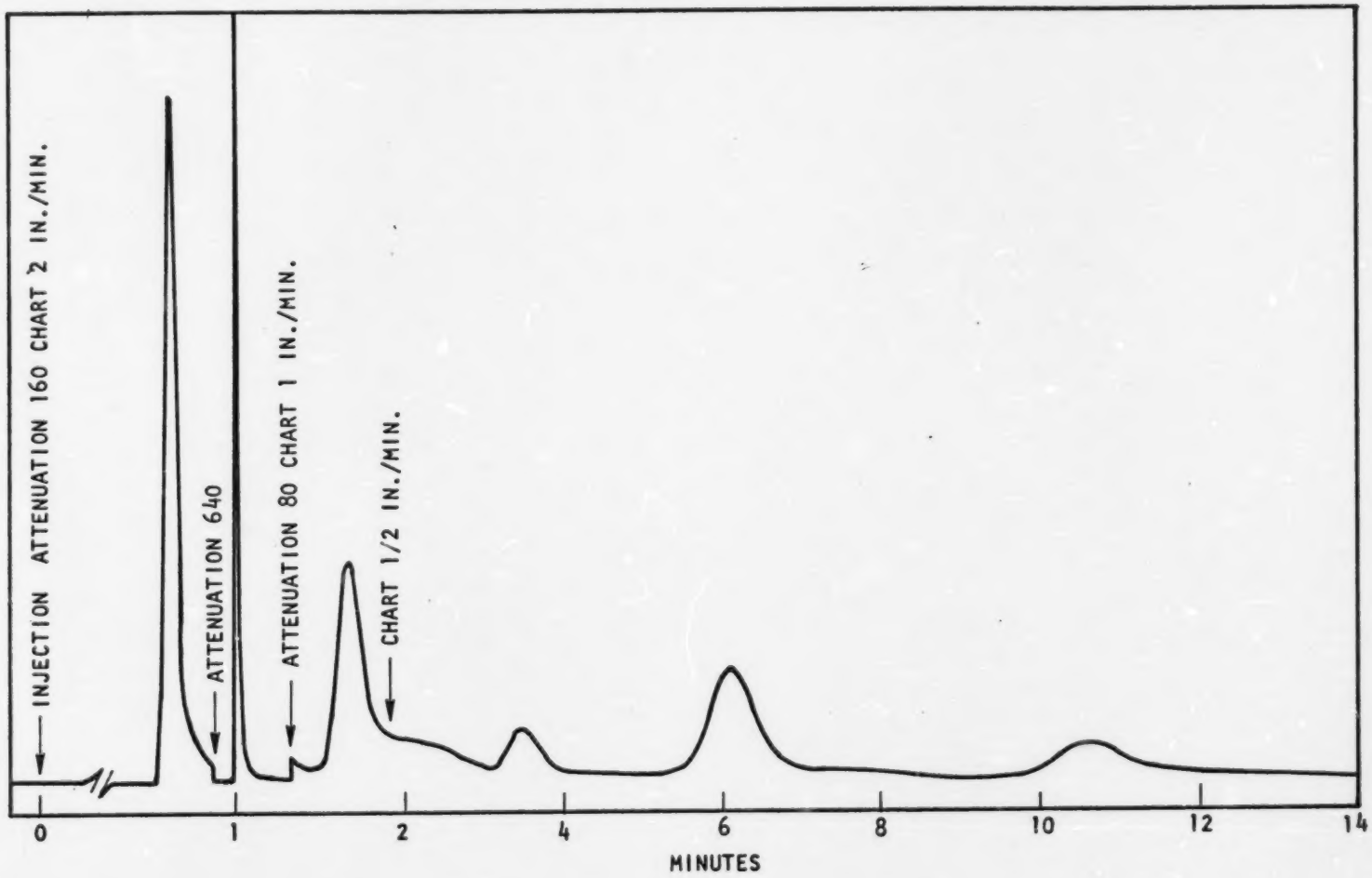

Figure 4. Pyrogram of 93 ppm Solution of Hexanoic Acid

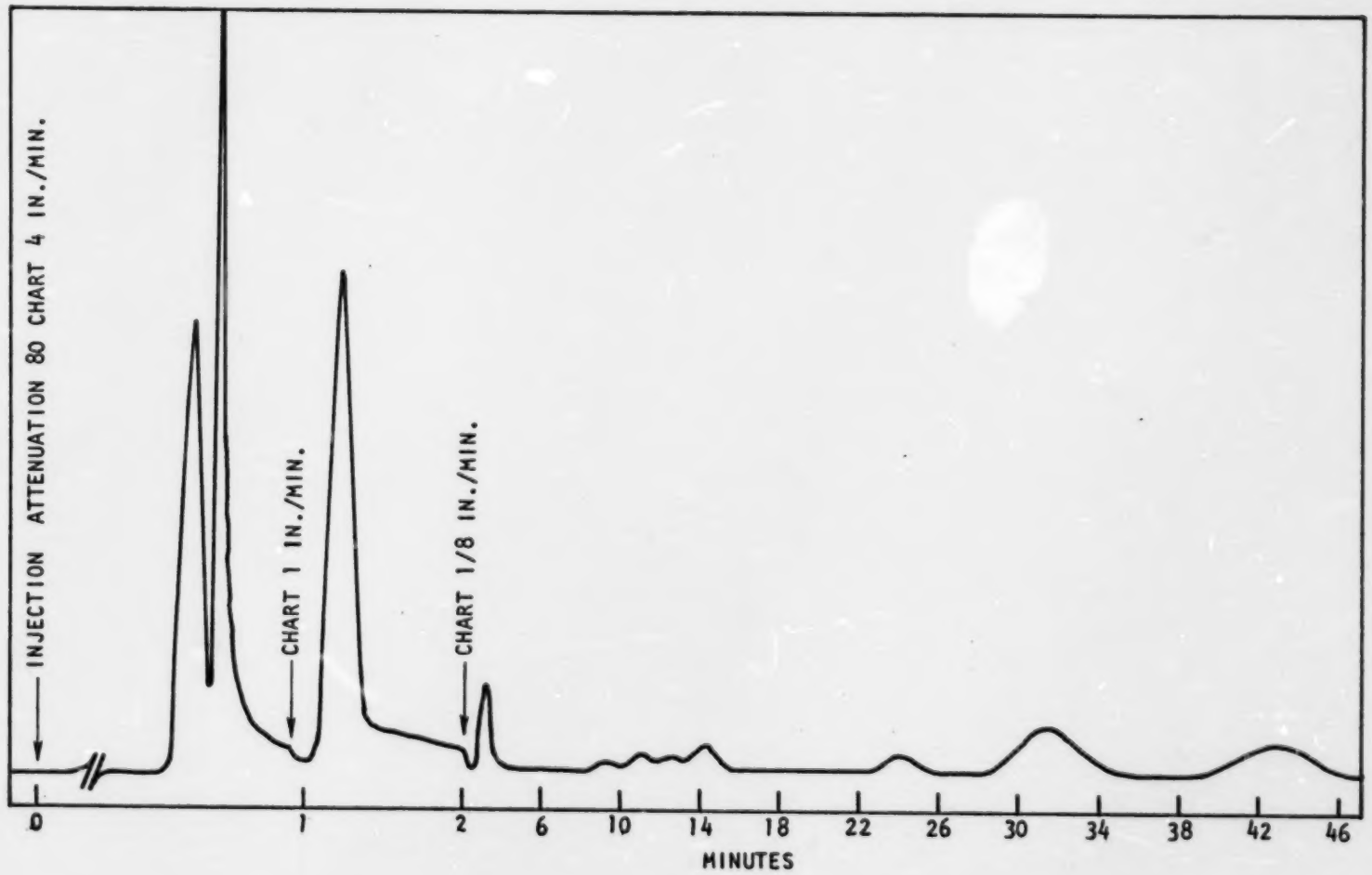

Figure 5. Pyrogram of 100 ppm dl-Valine in Water

A comparison of some of these current pyrograms with those available from the advanced pyrographic instrument showed that the breadboard model had a sensitivity of 50 to 100 times less than that for the advanced instrument. This sensitivity difference apparently results because a more sensitive electrometer and detector are used in the advanced pyrographic instrument. The low sensitivity, however, does not limit the potential use of the pyrographic methodology as it applies to the characterization of municipal wastes. Any gross effects which are observed can be readily analyzed for fine detail in more sensitive apparatus, if necessary.

PYROLYSIS OF MUNICIPAL WASTE

EXPERIMENTAL

Raw sewage, and primary, secondary, and tertiary treatment effluents were secured from the Pomona Water Renovation Plant for use in this program. The samples were collected in one-quart polyethylene bottles and then immediately frozen with dry ice. Preservation in the frozen state was maintained until pyrolysis was undertaken. At the time of pyrolysis, a sample was thawed, then homogenized in a high-speed blender, and placed in an ice bath to minimize biological activity. The raw sewage and the primary effluent needed the homogenization to reduce the settling of the solid matter. The samples of secondary and tertiary effluents, which did not contain solid matter, were treated in the same manner.

The previous instrumental conditions were used except the chromatographic column temperature was reduced to 110 C to provide better separation of the pyrographic peaks. During analysis, each sample was stirred each time before sampling with a syringe for injection into the breadboard pyrolytic apparatus. Each sample was initially pyrolyzed for one hour to establish the injection frequency that would provide a complete pyrogram showing all peaks. The time between injections was found to be one hour for the raw sewage, 30 minutes for the primary effluent, and 15 minutes for the secondary and tertiary effluents after which no additional peaks appeared. Then each sample was pyrolyzed several times to be certain that the pyrogram was representative and repeatable. Of each pyrogram, only the pertinent portion showing the observed peaks was reproduced in this report.

RESULTS AND DISCUSSION

The first set of samples was secured on 10 July 1969. The raw sewage, primary effluent, and secondary effluent were obtained from the new section of the Pomona Water Renovation Plant, and the tertiary effluent was secured from the advanced treatment plant. At the time of sampling, the solid matter in the raw sewage and primary effluent samples appeared to be uniformly distributed. The secondary and tertiary effluents appeared clear.

Pyrolysis of these samples yielded the pyrograms shown in Figures 6 through 9. In raw sewage (Figure 6), 13 peaks were observed. Of these, the major peaks had retention times of 0.80 and 1.22 minutes. Three other prominent peaks were present at 2.00, 4.3, and 7.7 minutes. In addition, a broad peak was present at 2.5 minutes and minor peaks were discernible at 0.98, 9.6, 11.0, 13.5, 16.6, 19.2, and 25 minutes.

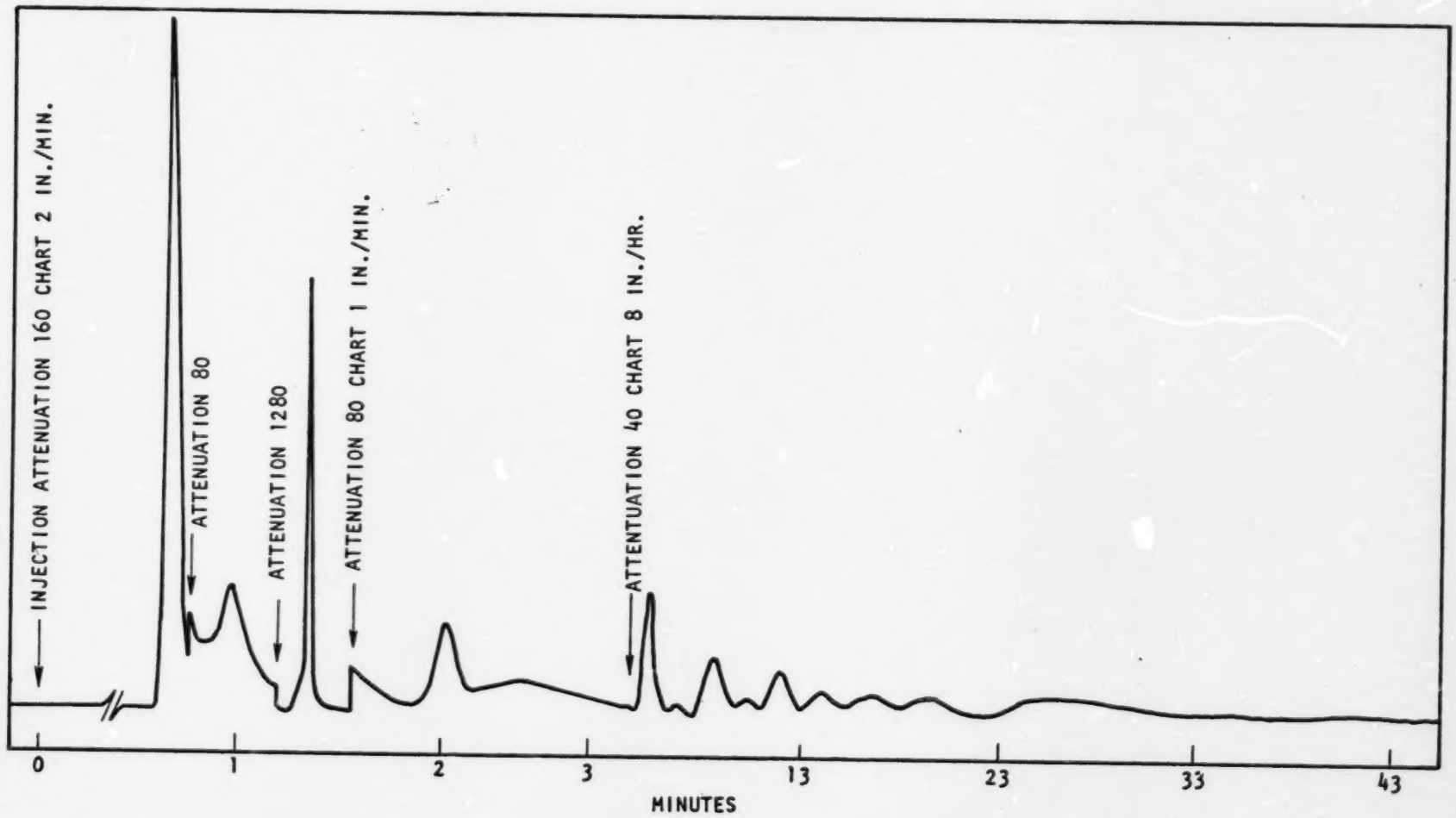

Figure 6. Pyrogram of Raw Sewage 10 July 1969

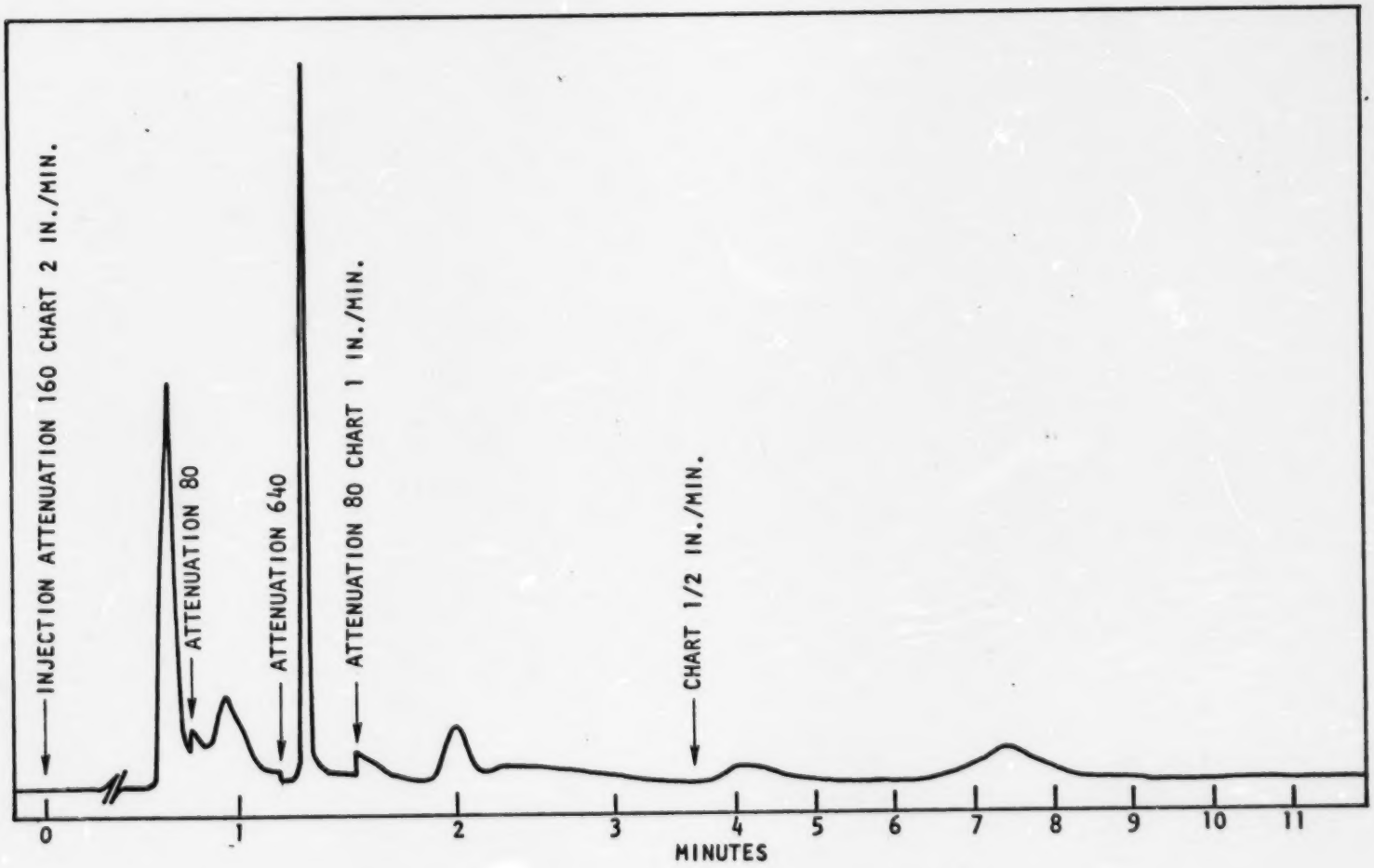

Figure 7. Pyrogram of Primary Effluent 10 July 1969

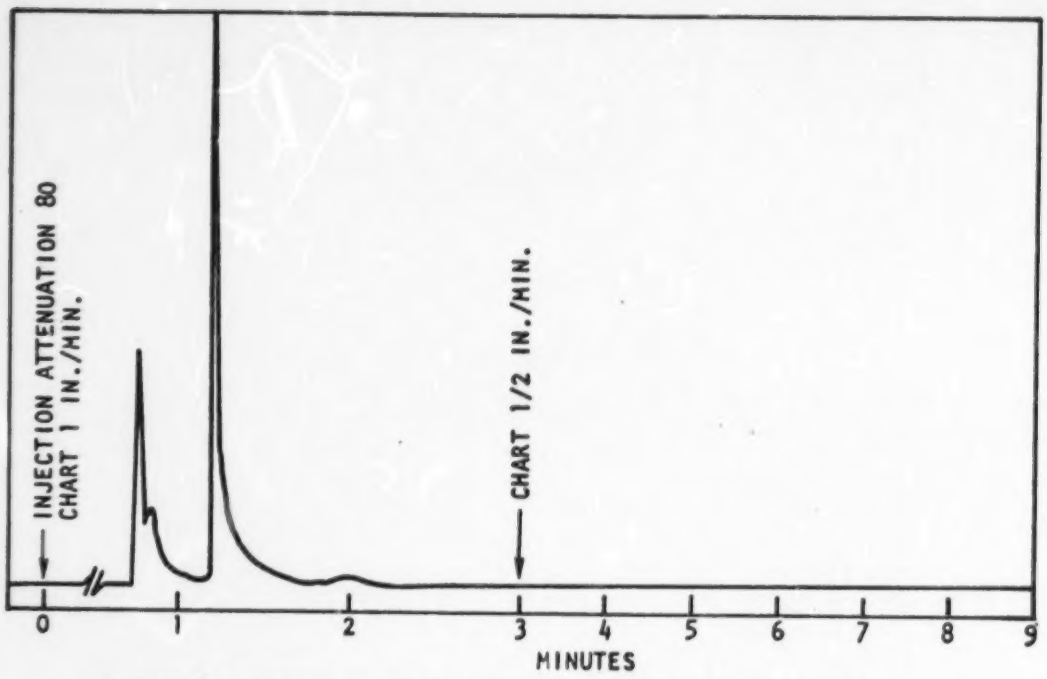

Figure 8. Pyrogram of Secondary Effluent 10 July 1969

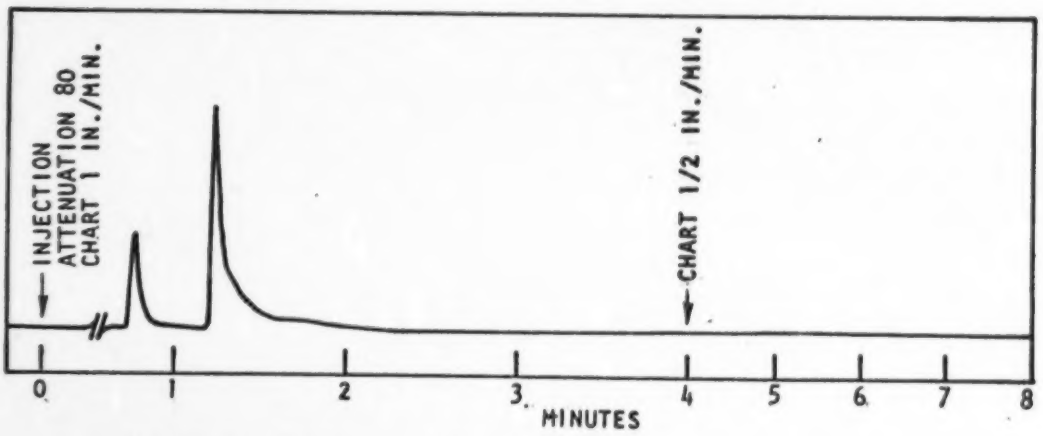

Figure 9. Pyrogram of Tertiary Effluent 10 July 1969

For the primary effluent, the pyrogram (Figure 7) had the two major peaks at 0.80 and 1.22 minutes. Minor peaks were present at 0.98, 2.00, 4.1, and 7.5 minutes. The pyrogram of the secondary effluent, shown in Figure 8, showed two major peaks at 0.80 and 1.22 minutes and two minor peaks at 0.90 and 2.00 minutes. In the pyrogram from the tertiary effluent (Figure 9), only the two peaks at 0.80 and 1.22 minutes were observed. The peaks in these pyrograms are summarized in Table I.

From examination of the pyrograms, it appears that some of the peaks are more persistent than others. These more persistent peaks may reflect lower rates of biodegradation for the waste materials contributing to such peaks.

The appearance of new peaks with retention times of 4.1 and 7.5 minutes in the primary effluent and a retention time of 0.90 minute in the secondary effluent is interesting. Each peak in a pyrogram may represent more than one compound. However, the appearance of new peaks does not necessarily imply formation of new compounds during the waste treatment. Minor shifts in retention time, such as from 4.3 (raw) to 4.1 (primary) minutes and 7.7 (raw) to 7.5 (primary) minutes, might be expected as a result of changes in composition ratios of the organic materials as the raw sewage undergoes primary treatment.

On 16 July 1969, a second set of samples of raw sewage, primary effluent, and secondary effluent was obtained from the old section of the Pomona Water Renovation Plant. At the same time, a sample of tertiary effluent was obtained from the advanced treatment plant which was operating on the secondary effluent from the old section of the renovation plant. From visual observations, the secondary and tertiary effluents were very clear. The solid matter in the primary effluent appeared to be uniformly distributed. The raw sewage in the tanks, however, was non-homogeneous in appearance.

This second set of samples was pyrolyzed in the same manner as before. The pyrograms of these samples are shown in Figures 10 through 13 and the pyrographic peaks are summarized in Table II. For the raw sewage, the pyrogram shown in Figure 10 was obtained. In this pyrogram, two major peaks at 0.80 and 1.22 minutes, three prominent peaks at 2.00, 4.3, and 7.7 minutes, a broad peak at 2.5 minutes, and minor peaks at 0.98, 1.02, 9.6, 11.0, 12.7, 15.0, 18.6, 24, 34, and 43 minutes were observed. The primary effluent gave a pyrogram (Figure 11) with two major peaks at 0.80 and 1.22 minutes. Several minor peaks were present at 0.98, 2.00, 2.5, 4.1, and 7.5 minutes. The pyrogram (Figure 12) for the secondary effluent shows the major peaks at 0.80 and 1.22 minutes and a small peak at 0.90 minute. The tertiary effluent gave a pyrogram, shown in Figure 13, with only two peaks which had retention times of 0.80 and 1.22 minutes.

TABLE I

RETENTION TIMES OF PYROGRAPHIC PEAKS FOR POMONA
WATER RENOVATION PLANT SAMPLES SECURED ON 10 JULY 1969

Retention Time, Minutes	Raw Sewage	Primary Effluent	Secondary Effluent	Tertiary Effluent
0.80	X	X	X	X
0.90			X	
0.98	X	X		
1.22	X	X	X	X
2.00	X	X	X	
2.5	X			
4.1		X		
4.3	X			
7.5		X		
7.7	X			
9.6	X			
11.0	X			
13.5	X			
16.6	X			
19.2	X			
25	X			

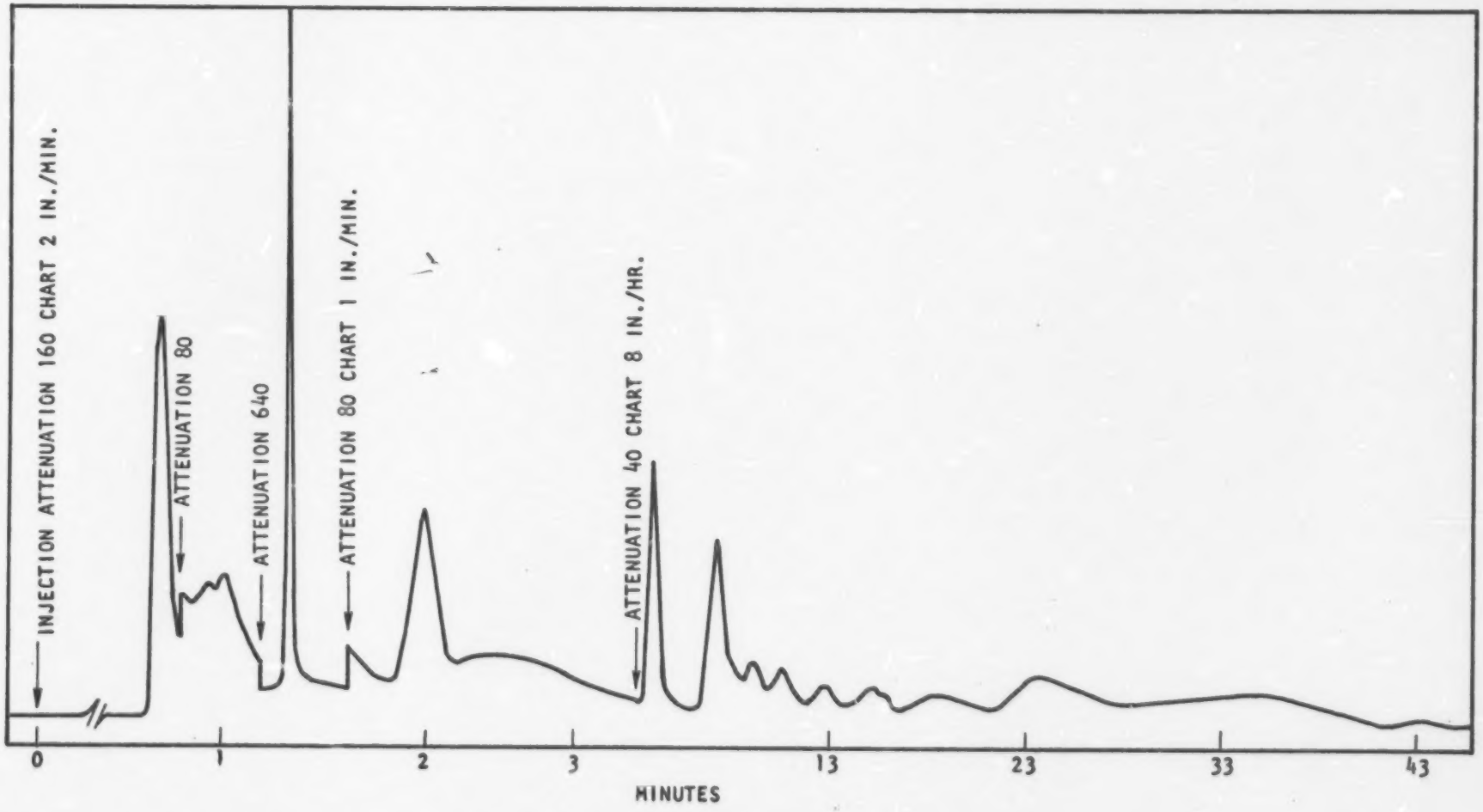

Figure 10. Pyrogram of Raw Sewage 16 July 1969

Figure 11. Pyrogram of Primary Effluent 16 July 1969

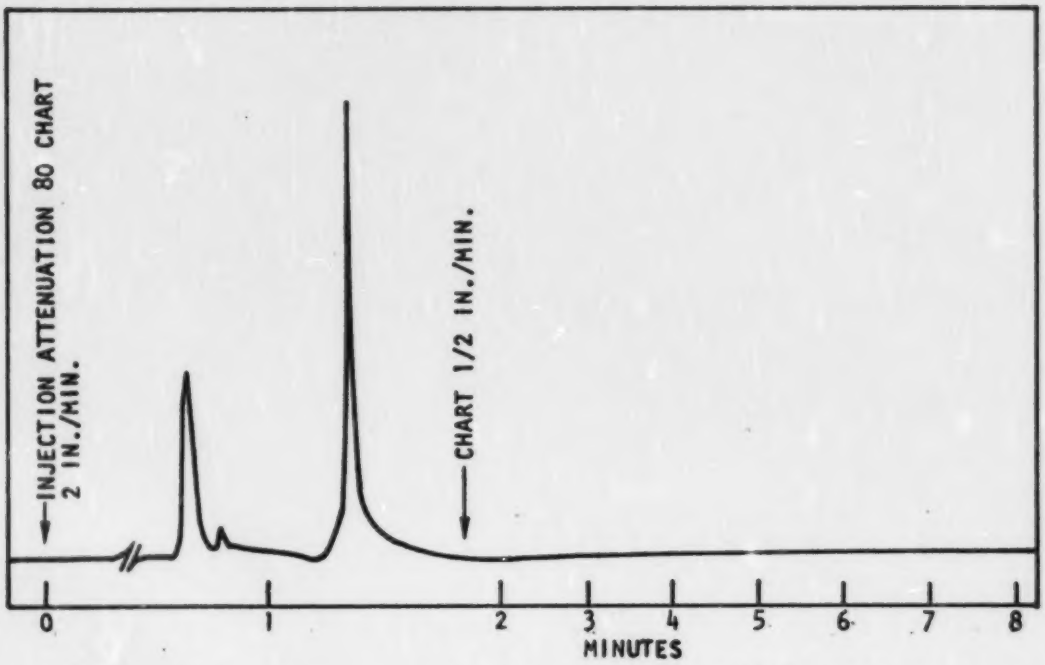

Figure 12. Pyrogram of Secondary Effluent 16 July 1969

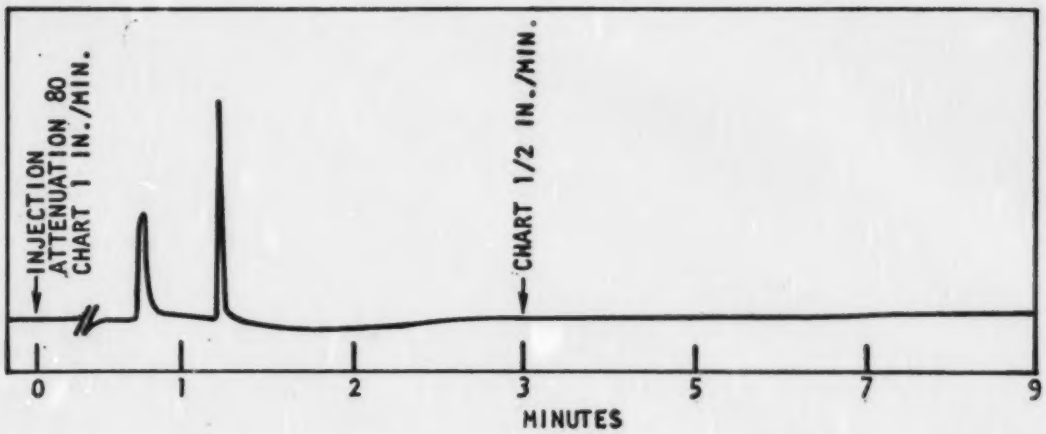

Figure 13. Pyrogram of Tertiary Effluent 16 July 1969

TABLE II

RETENTION TIMES OF PYROGRAPHIC PEAKS FOR POMONA
WATER RENOVATION PLANT SAMPLES OBTAINED ON 16 JULY 1969

Retention Time, Minutes	Raw Sewage	Primary Effluent	Secondary Effluent	Tertiary Effluent
0.80	X	X	X	X
0.90			X	
0.98	X	X		
1.02	X			
1.22	X	X	X	X
2.00	X	X		
2.5	X	X		
4.1		X		
4.3	X			
7.5		X		
7.7	X			
9.6	X			
11.0	X			
12.7	X			
15.0	X			
18.6	X			
24	X			
34	X			
43	X			

These pyrograms are similar to those for the samples secured on 10 July 1969. As before in the other set of pyrograms, new peaks occurred in the analysis of these primary and secondary effluents. These peaks could have originated from changes in ratios of the waste materials represented by the peaks. However, the possibility of formation of new compounds during the waste treatment process being the origin of the new peaks cannot be ruled out.

For each sample obtained on both dates, the organic load expressed as BOD equivalent was calculated according to a procedure reported elsewhere (5). With one exception, the organic load of each sample, given in Table III, is in the range of values obtained for similar type samples over a period of time at the Hyperion Treatment Plant. The exception is the raw sewage secured on 16 July 1969. The high value, 929 mg/liter, for this sample apparently resulted from the nonhomogeneity of the raw sewage in the tanks. At the time of sampling, there was considerable grease, scum and solid matter floating on the water surface which made it difficult to obtain a representative sample.

It is not known to what extent the solids contribute to the pyrogram of a raw sewage. To obtain a partial answer to this question, the raw sewage secured on 16 July 1969 was thawed, homogenized, and then enriched by centrifuging. The supernatant was decanted to give an aqueous solution enriched with the solid matter. The volume of this enriched sewage was approximately one-sixth of the original raw sewage. A pyrogram of this enriched sewage is shown in Figure 14 and a comparison of the pyrographic peaks with those of the raw sewage is given in Table IV. With the exception of the third peak, the first 9 peaks in the pyrogram of the raw sewage (Figure 10) are found in the enriched sewage pyrogram (Figure 14). The remainder of the pyrogram for the enriched sewage differs in some respects from the raw sewage pyrogram. Although the enriched sewage pyrogram is generally similar to the pyrogram for raw sewage, the retention times of peaks differ and the magnitudes of the peaks are not proportionally larger in all cases.

TABLE III

CALCULATED ORGANIC LOAD FOR PYROLYZED MUNICIPAL WASTE SAMPLES

	Organic Load Expressed as BOD Equivalent, mg/l	
Sample	July 10	July 16
Raw Sewage	454	929
Primary Effluent	173	203
Secondary Effluent	36	15
Tertiary Effluent	18	7

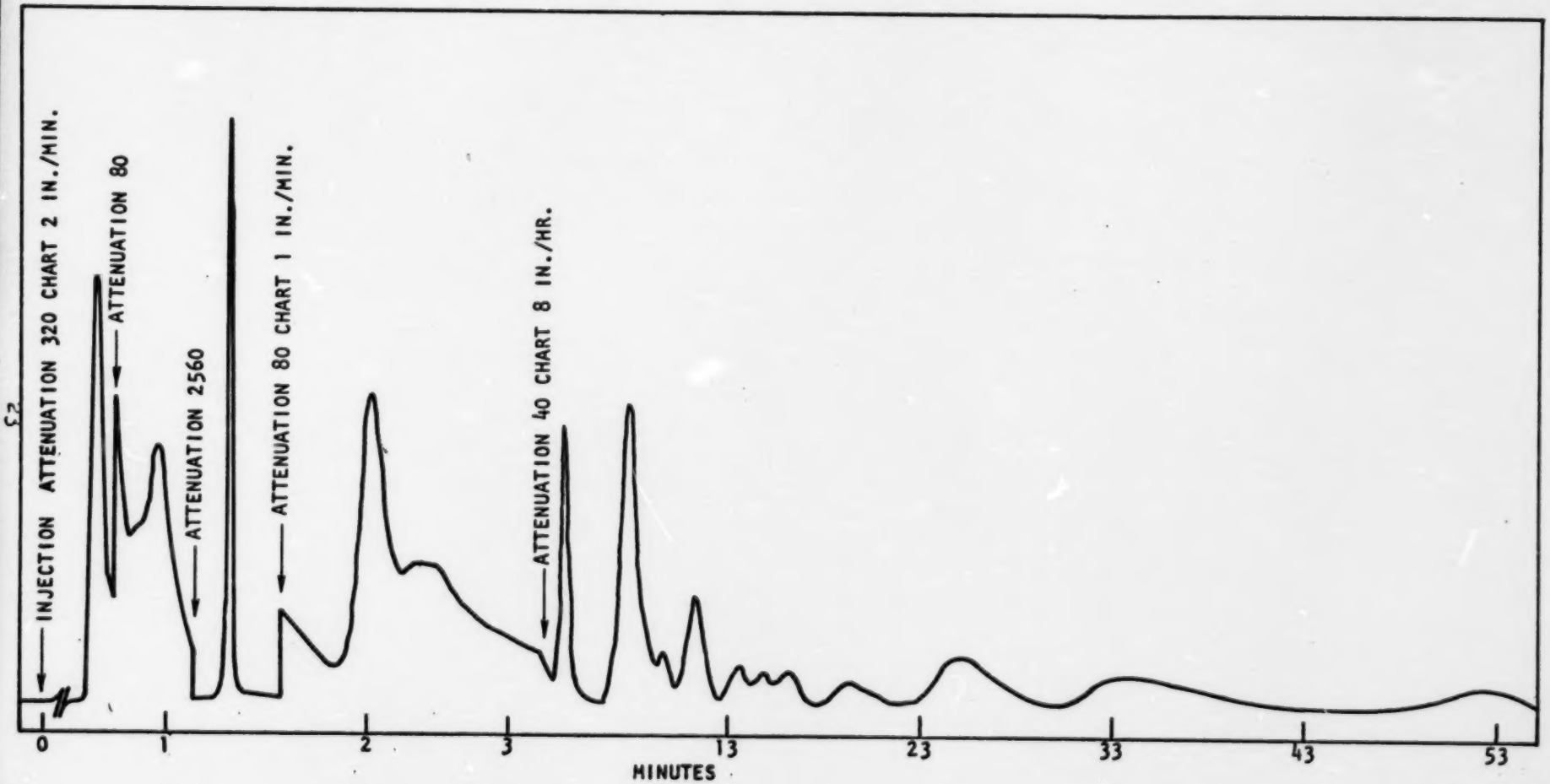

Figure 14. Pyrogram of Enriched Sewage 16 July 1969

TABLE IV

COMPARISON OF PYROGRAPHIC PEAKS FOR RAW SEWAGE AND ENRICHED SEWAGE

Retention Time, Minutes	Raw Sewage	Enriched Sewage
0.80	X	X
0.98	X	X
1.02	X	
1.22	X	X
2.00	X	X
2.5	X	X
4.3	X	X
7.7	X	X
9.6	X	X
11.0	X	
11.3		X
12.7	X	
13.5		X
15.0	X	X
16.0		X
18.6	X	
19.2		X
24	X	
25		X
34	X	X
43	X	
52		X

CONCLUSIONS AND RECOMMENDATIONS

The results of this limited three-month study indicate that:

1. The pyrographic traces obtained for raw sewage, and primary, secondary, and tertiary waste effluents are reproducible and specific to each material.

2. A predictable reduction in the overall intensity of the pyrographic peaks takes place as the raw sewage passes through the various waste treatment processes, reflecting a decrease in the organic content.

3. Some peaks are more persistent than others, suggesting different rates of biodegradation for the various organic materials comprising the waste.

4. New peaks appear in the pyrograms of the primary and secondary effluents. The appearance of peaks with new retention times may be due to changes in composition within materials represented by a peak. Such changes could be due to different rates of biodegradation or to formation of new compounds as a product of biodegradation.

It is apparent that the limited scope of the program did not permit the technique to be exploited sufficiently to assess its ultimate usefulness to the analysis of waste. However, the appearance of new peaks and the shift in peak retention times indicate that differentiation among different compounds or complex mixtures may be possible with increased pyrogram resolution. Therefore, it is recommended that the technique be further explored, by means of pyrographic instrumentation having increased sensitivity, to determine its ultimate usefulness in analysis of wastewater.

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